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# Enhanced probabilities of phonon-assisted optical transitions in semiconductor quantum dots

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**Abstract.** A theory of phonon-assisted optical transitions in semiconductor quantum dots is developed which takes into account non-adiabaticity of the exciton-phonon system. The role of non-adiabaticity is shown to be of paramount importance in spherical quantum dots, where the lowest one-exciton state can be degenerate or quasi-degenerate. In quantum dots of lower symmetry, the effects of non-adiabaticity reveal themselves mainly due to the phonon-induced mixing of states, which belong to different energy levels. Our approach is applied to explain the optical spectra of several quantum-dot structures: ensembles of spherical CdSe, $CdSe_xS_{1-x}$ and PbS quantum dots, self-assembled InAs/GaAs and CdSe/ZnSe quantum dots, brick-shaped InAs/GaAs quantum dots.

## Introduction

The interest in the optical properties of quantum dots is continuously growing because of the great prospects of these structures for optoelectronic applications. Numerous experiments, e. g., recent measurements [1–5] of photoluminescence of self-assembled InAs/GaAs quantum dots reveal a remarkably high probability of the phonon-assisted transitions. Attempts to interpret some of these experiments on the basis of the adiabatic theory meet considerable difficulties. Thus, for spherical CdSe quantum dots, the Huang-Rhys parameter $S$ takes values, which appear to be significantly (by one or two orders of magnitude) smaller than the so-called experimental values of the Huang-Rhys parameter, $S_{\rm exp}$, derived from the ratio of the measured intensities of the phonon satellites. In the framework of the adiabatic approach, various mechanisms, which ensure separation of the electron and hole pair in space [3, 6, 7], are commonly considered as a possible origin for the increased Huang-Rhys parameter. We show that the proposed non-adiabatic treatment of phonon-assisted optical transitions can provide an explanation for the remarkably high intensities of phonon satellites observed in the photoluminescence and Raman spectra of various quantum-dot structures.

## 1. Photoluminescence spectra of quantum dots

The adiabatic approach [8, 9] supposes that (i) both the initial and final state for a quantum transition are non-degenerate, (ii) energy differences between the electron (exciton) states are much larger than the phonon energies. We have revealed, that these conditions are often violated for optical transitions in quantum dots. In other words, we emphasize, that the exciton-phonon system in a quantum dot can be essentially *non-adiabatic*. There can

[1] In collaboration with V. M. Fomin, V. N. Gladilin, E. P. Pokatilov, S. N. Klimin, and S. N. Balaban

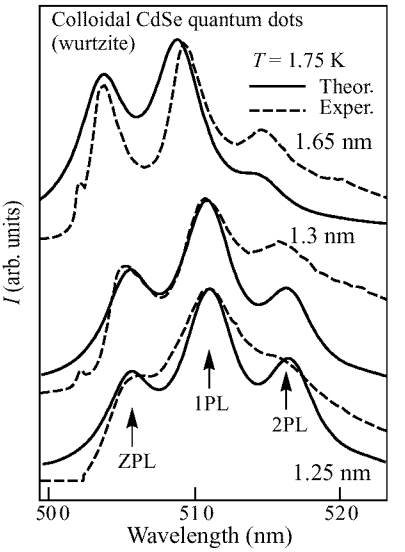


**Fig. 1.** Fluorescence spectra of spherical CdSe quantum dots with wurtzite structure at various average radii $\langle R \rangle$. Dashed curves represent the experimental data [11]. Solid curves are calculated within non-adiabatic approach (see Ref. [12]).

be two cases: the interaction of an exciton in a degenerate state with phonons results in *internal non-adiabaticity* (the proper Jahn–Teller effect), while the existence of exciton levels separated by an energy comparable with the LO-phonon energy leads to *external non-adiabaticity* (the pseudo Jahn–Teller effect) [10].

In Figure 1, we show the photoluminescence spectra of spherical CdSe quantum dots with various average radii. For the measured $K$-phonon-peak intensities, $I_K$, the ratios $I_1/I_0$ and $2I_2/I_1$ obviously differ from each other. In other words, the observed phonon-peak intensities obey a serial low, which significantly deviates from the Franck–Condon progression. Solid curves in Fig. 1 represent the photoluminescence spectra calculated within the non-adiabatic approach developed in Ref. [12]. As seen from Fig. 1, taking into consideration the effects of non-adiabaticity provides an adequate description of the observed phonon-peak intensities as well as their dependence on the size of quantum dots.

As shown in Ref. [12], the photoluminescence spectra of quantum dots can be strongly affected by the processes of phonon emission in the course of absorption of the exciting radiation. In Ref. [13] we have calculated the optical spectra of brick-shaped InAs/GaAs quantum dots created by AFM-mediated local anodic oxidation. For ensembles of those quantum dots with relatively narrow size distributions, the aforementioned processes appear to provide a dominant contribution to the intensities of phonon satellites in the spectra of resonant photoluminescence.

Figure 2 illustrates the crucial role of the non-adiabaticity effects on the phonon-assisted light absorption by InAs/GaAs self-assembled quantum dots. We have modeled the quantum-dot structure by an InAs cylinder of height $h$ and radius $R$ embedded into GaAs. The absorption spectrum is calculated taking into account the four lowest energy levels of an electron-hole pair. The results shown in Fig. 2 imply that, due to the effects of non-adiabaticity, a significant enhancement of phonon-satellites intensities must occur also in photoluminescence spectra of self-assembled quantum dots.

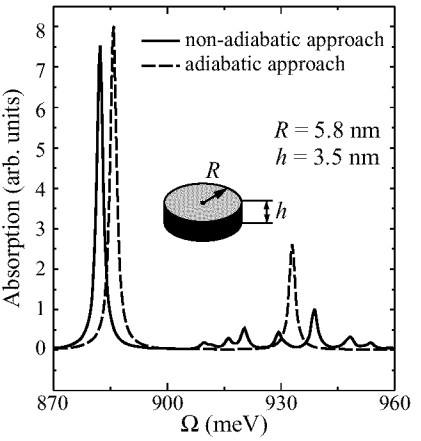


**Fig. 2.** The absorption spectra of a cylindrical InAs quantum dot calculated within the adiabatic and non-adiabatic approaches.

The triplet structure of the first phonon replica, recently observed in the photoluminescence spectra of self-assembled CdSe/ZnSe quantum dots structures [14], is interpreted [15] in terms of resonant relaxation of excitons with participation of optical phonons. The optical-phonon modes specific to these nanostructures are: (i) CdSe-like modes confined to the quantum dot, (ii) spatially extended CdSe-like and ZnSe-like modes. In Figure 3, our theoretical results for the phonon-assisted photoluminescence spectra are shown for two ensembles of cylindrical CdSe quantum dots. Within each ensemble, the quantum dots have a fixed height $h$ and various diameters $d$. Three most pronounced peaks, which belong to the first phonon replica in the measured photoluminescence spectra of CdSe quantum dots [14], can be attributed to spatially extended ZnSe-like phonon modes, to localized CdSe-like modes and to spatially extended CdSe-like modes (in order of increasing detec-

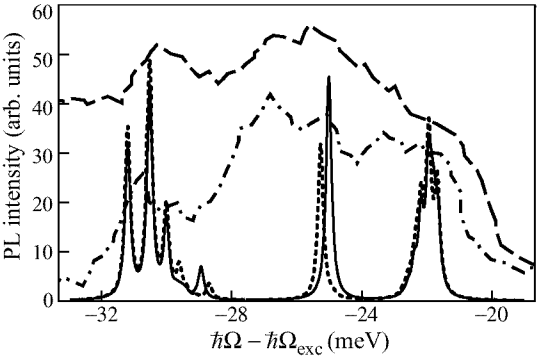


**Fig. 3.** Photoluminescence spectra [15] of CdSe quantum dots with height $h = 2$ nm (solid curve) and $h = 1.8$ nm (dotted curve) on a 2ML remnant layer, as calculated within the present theory, compared to the experimental data for a CdSe quantum dot structure formed by thermally activated surface reorganization of an initially uniform 3 ML CdSe film (after Lowisch *et al.* [14]). The dashed and dash-dot curves correspond to the excitation energies $\hbar\Omega_{\text{exc}} = 2.495$ eV and $\hbar\Omega_{\text{exc}} = 2.465$ eV, respectively. For clarity, the experimental spectra have been shifted along the ordinate.

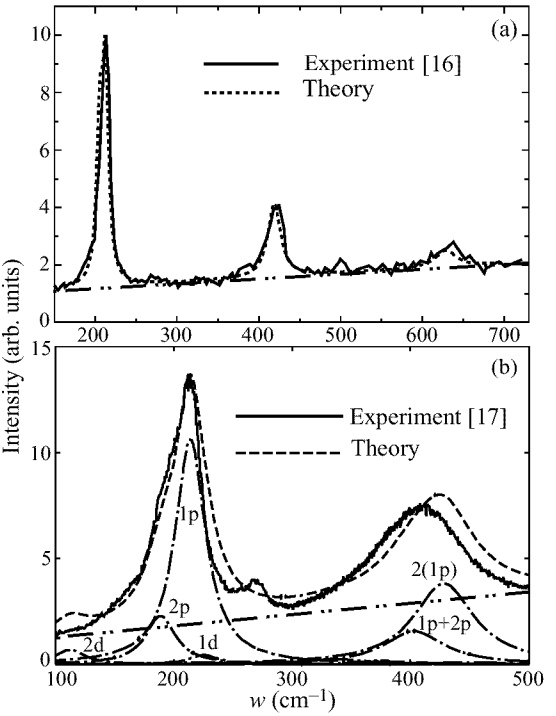


**Fig. 4.** Resonant Raman scattering spectra of an ensemble of CdSe quantum dots with average radius 2 nm (panel *a*) and of PbS quantum dots with average radius 1.5 nm (panel *b*). The dash-dot-dot curves show the luminescence background. The dash-dot curves in panel *b* indicate contributions of phonon modes (classified in analogy with electron states in a hydrogen atom) into the Raman spectrum.

tion energy $\hbar\Omega$). The calculated positions and the relative heights of the peaks induced by spatially extended ZnSe- and CdSe-like phonon modes are in a fair agreement with the experimental data [14]. The experimental peaks, which can be related to localized phonons, are characterized by a rather large frequency spread when compared with the theoretically calculated peaks. This may be due to inhomogeneous strain distribution as well as to fluctuations of the chemical composition in the experimental samples.

## 2. Raman scattering in quantum dots

Since the electron-phonon coupling constant $\alpha$ in the quantum dots under consideration is relatively small ($\alpha < 1$), the $K$-phonon Raman scattering intensity, corresponding to a definite combinatorial frequency $\sum_{j=1}^{K} \omega_{\nu_j}$, can be analyzed to the lowest ($K$-th) order in $\alpha$. The scattering intensity is then expressed through a squared modulus of the scattering amplitude:

$$F_K^{(\pm)}(\nu_1, \ldots, \nu_K) = \sum_{\mu_0,\ldots,\mu_K} \frac{d^I_{\mu_0}\left(d^S_{\mu_K}\right)^*}{\tilde{\omega}_{\mu_0} - \Omega_I + i\tilde{\Gamma}_{\mu_0}}$$

$$\times \prod_{j=1}^{K} \langle \mu_j | \hat{\beta}_{\nu_j} | \mu_{j-1} \rangle \left[ \tilde{\omega}_{\mu_j} - \Omega_I \pm \sum_{k=1}^{j} \left( \omega_{\nu_k} \pm i\Gamma_{\nu_k} \right) + i\tilde{\Gamma}_{\mu_j} \right]^{-1}.$$

Here $\tilde{\omega}_\mu$ is the transition frequency and $d_\mu^{I(S)} \equiv \langle\mu|\hat{d}^{I(S)}|0\rangle$ is the dipole matrix element for a transition from the exciton vacuum to the eigenstate $|\mu\rangle$ of the exciton Hamiltonian, $\tilde{\Gamma}_\mu$ is the inverse lifetime of an exciton in the state $|\mu\rangle$, $\Gamma_\nu$ is the inverse lifetime of a phonon of the mode $\nu$. The exciton-phonon interaction amplitude, $\hat{\beta}_\nu = \hat{\gamma}_\nu(\mathbf{r}_e) - \hat{\gamma}_\nu(\mathbf{r}_h)$, is determined by the amplitudes of the electron-phonon and hole-phonon interaction. $\mathbf{r}_e$ and $\mathbf{r}_h$ are the coordinates of an electron and of a hole, respectively. It is worth noting, that the above equation is not based on the adiabatic approximation and takes into account both the Jahn–Teller and pseudo-Jahn–Teller effects. The calculated by us Raman spectra for CdSe and PbS quantum dots (see Fig. 4) show an excellent agreement with experimental results [16, 17].

The effects of non-adiabaticity result in selection rules for the Raman scattering, which differ essentially from those derived within the adiabatic approximation. Owing to a considerable LO-phonon dispersion in the bulk material, Raman peaks are easily identified. The main contribution into both fundamental and overtone bands is due to $1p$- and $2p$-phonons, while the adiabatic approach would imply a domination of peaks corresponding to $s$-phonons.

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